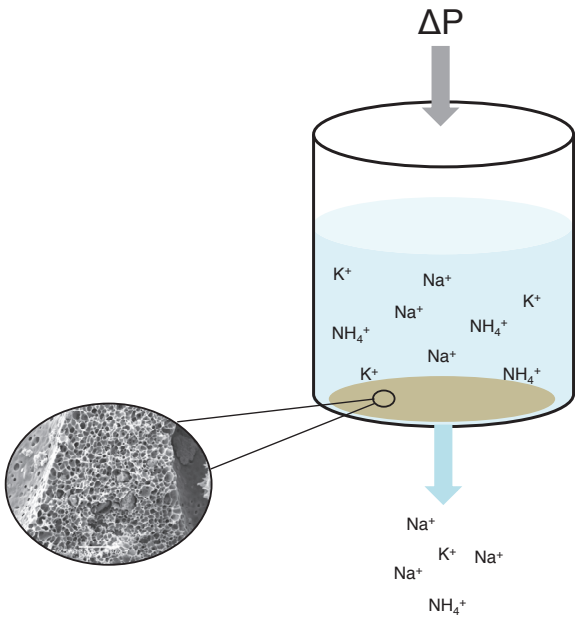
Ion-selective membranes for the recovery of ammonium and potassium

Casadella Muni, Anna

Clinoptilolite-based mixed matrix membranes for the selective recovery of ammonium and potassium



Abstract

A clinoptilolite-based mixed matrix membrane (MMM) was developed and studied for the selective recovery of ammonium and potassium. Adsorption of sodium (Na^+), potassium (K^+) and ammonium (NH_4^+) was investigated with single salt and equimolar salt mixture under static and dynamic conditions. Furthermore, the adsorption capacity of clinoptilolite was investigated when embedded in the MMM and in fine-grained form. Two conditioning methods were compared: HCl and NaCl. Conditioned clinoptilolite with NaCl gave higher static adsorption capacities than with HCl which alters the chemical structure of clinoptilolite. The adsorption of Na^+ was not detected in the static adsorption experiments and results showed that Na^+ adsorbed during the conditioning process was exchanged by K^+ and NH_4^+. The clinoptilolite embedded in MMM reduced the porosity of the MMM so the highest adsorption capacity was reached when the amount of polymer was the lowest: 30wt.% polymer and 70wt.% clinoptilolite. The application of MMM in a dead-end filtration cell (dynamic adsorption) resulted in higher adsorption capacities compared to static conditions and comparable results between synthetic solutions and diluted urine samples. This indicates that MMM is a suitable method for the recovery of K^+ and NH_4^+ directly from a diluted urine matrix. The desorption (recovery) of K^+ and NH_4^+ from MMM was higher using water at 60°C than using an acidic treatment.

Keywords: clinoptilolite; mixed matrix membrane; adsorption capacity; nutrient recovery; sodium removal

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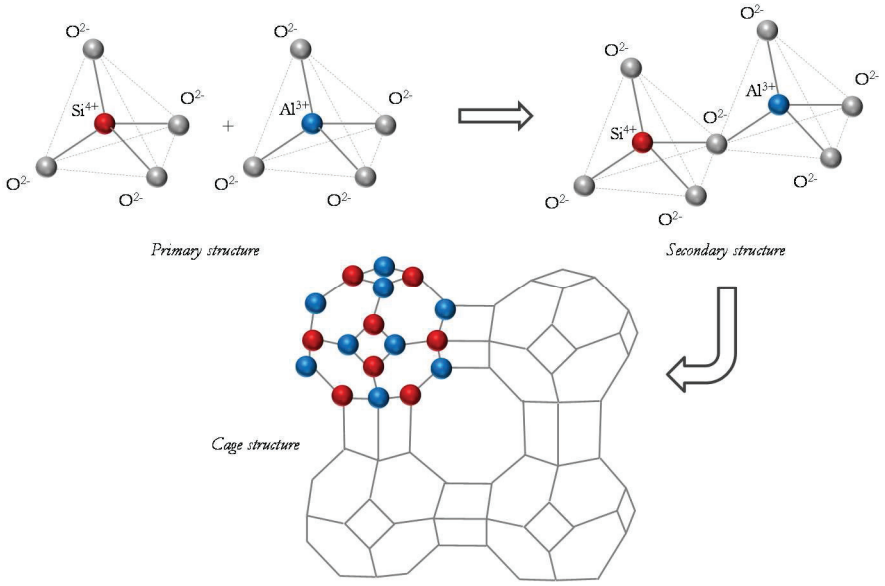
2.1 Introduction

Our planet is expecting a population growth in the coming years leading to a higher demand of food production (i.e., crops) that will require higher crop yields [1]. Natural (e.g. manure) or synthetic fertilizers are used to guarantee sufficient growth of crops. Currently, fertilizer production relies on scarce resources [2] and/or energy intensive processes [3]. In order to make fertilizer production more sustainable, recent studies are focusing on exploiting wastewater such as urine as an alternative resource [2, 4-6]. In urine, the main cations are: sodium (Na^+), potassium (K^+), ammonium (NH_4^+) [7]. K^+ and NH_4^+ could be recovered from urine and used as a natural fertilizer [8]. However, a Na^+ concentration in soil higher than 36mM NaCl is toxic and could lead to death of the crops [9]. Therefore, it is necessary to separate Na^+ from K^+ and NH_4^+ prior to application as fertilizer. Na^+ cannot be separated from K^+ and NH_4^+ based on charge, size exclusion or diffusivity as the cations have the same charge (+1) and very similar hydrated radii [10] and diffusion coefficient [11].

It has been demonstrated [12-17] that ion-exchange using natural zeolites is an alternative method for the removal (adsorption in the zeolite) and recovery (desorption from the zeolite) of NH_4^+ and K^+ from wastewater. More specifically, some research has been carried out on the feasibility and on the required conditions for the use of clinoptilolite to remove and recover NH_4^+ from human urine [17, 18]. Clinoptilolite is an inexpensive abundant natural zeolite in the form of alumino-silicate minerals with ion sieving properties and high cation-exchange capacity (CEC). The generic chemical formula of clinoptilolite is $(Na,K,Ca)_6(Si,Al)_{36}O_{72}\cdot 2H_2O$. Clinoptilolite is composed by a three-dimensional framework of SiO_4 and AlO_4 forming tetrahedral ring channels that provide ion sieving properties (Scheme 1). The ion-exchange capacity of clinoptilolite is explained through its chemical composition. Al^{3+}

generally occupies the position in the center of the tetrahedron of four oxygen atoms, the isomorphous replacement of Al^{3+} with Si^{4+} (common in silicates) provides a negative charge in the inner part of the structure (lattice) [19]. Therefore, each replacement of Al^{3+} with Si^{4+} requires a cation (e.g. alkali metal ions) to maintain the overall electroneutrality in the lattice. Given a higher selectivity of clinoptilolite for K^+ and NH_4^+, these cations can be exchanged with the ions already adsorbed [15, 20]. The application of clinoptilolite for separation purposes has been mainly focused on fixed, fluidized and expanded beds. However, these technologies have drawbacks such as pressure drop over the column and compaction that prevent the system to work at its full potential [21, 22]. These drawbacks are not exclusive for clinoptilolite, they are well-known for other adsorbents, for example peptides (e.g. pentadecapeptide) to separate proteins [23, 24]. As Avramescu *et al.* [25] pointed out, the optimal column would have an infinitely short bed height to minimize pressure drops and an infinite width to maximize the ion-exchange efficiency. Thus, there is the need to investigate an alternative to column-based technologies to overcome their drawbacks and achieve a more efficient removal and recovery.



Scheme 1. Composition of the cage structure of clinoptilolite.

Mixed matrix membranes (MMM) allow the fixation of ion-exchanger (adsorbent) and are thin enough and porous to avoid pressure drops. MMM are a solid–solid system comprised of inorganic dispersed phase inserted in a polymer matrix. The inorganic dispersed phase (e.g. zeolite) provides selectivity due to its specific chemical structure. The polymer matrix grants mechanical support [26]. MMM were first used for the separation of two gases (CO_2 and CH_4) in 1970s by Paul and Kemp [27] using 5A zeolite as adsorbent and polydimethylsiloxane (PDMS) as polymer. Since then, MMM are vastly [28] used in gas separation processes. Moreover, they also find applications in liquid solutions for example in enzyme [29] or protein [30] separation.

In this study, we propose an alternative to column-based technologies to separate and recover K^+ and NH_4^+ from a diluted urine matrix. We studied the adsorption capacity of clinoptilolite in form of clay and embedded in MMM for the separation of Na^+ from K^+ and NH_4^+. Furthermore, we studied the recovery (desorption) of K^+ and NH_4^+. We demonstrate an improvement in

ion-exchange capacity of K^+ and NH_4^+ when MMM are operated under pressure-driven conditions using a synthetic solution and a diluted urine matrix.

2.2 Experimental

2.2.1 Materials

Clinoptilolite extracted from a large sedimentary deposit in Croatia was purchased from Zeocare (The Netherlands). Polysulfone (PSf) with a molecular weight of 75kDa and Polyvinylpyrrolidone (PVP) with a molecular weight of 3.5kDa were obtained from Acros Organics (The Netherlands) and used without further purification. 1-Methyl-pyrrolidinone (NMP, Sigma Aldrich) was employed as solvent for the casting solution. High purity grade chemicals, hydrochloric acid (HCl, 37%), sodium chloride (NaCl), sodium nitrate ($NaNO_3$), potassium nitrate (KNO_3) and ammonium nitrate (NH_4NO_3), were supplied by Sigma Aldrich and were used without further purification. Human urine from a healthy individual was collected 1h in a beaker prior to the start of the experiments. We used fresh urine to avoid the hydrolysis of urea [31], so to avoid a change of NH_4^+ concentration in time. Solutions were prepared using ultrapure water (Millipore purification unit).

2.2.2 Adsorbent

Clinoptilolite was described by the distributors as 40-50% pure. The impurities included montmorillonite, feldspar, calcite, quartz and halite. The chemical composition of the clinoptilolite was stated by the distributor as in Table 1.

Table 1. Chemical composition of purchased clinoptilolite.

Component	% (-)
SiO_2	55.8
Al_2O_3	13.3
CaO	5.75
Na_2O	3.90
K_2O	2.35
Fe_2O_3	1.30
MgO	0.70
Loss of ignition	17.0

Adsorbent preparation

Clinoptilolite was washed for 10 minutes with demineralized water to remove fine particles. After drying the zeolite at 100°C for 24h, it was grinded by a ball mill grinder (Retsch, The Netherlands) at 450rpm for 30 minutes. Longer grinding times (1h and 3h) were tested and they resulted in the same range of particle size (0.5-10μm; DIPA2000 particle size analyser, Eyetech, Ankersmid, The Netherlands). The grinded zeolite (fine grain) was afterwards conditioned with 1M HCl or 1M NaCl to exchange prior adsorbed cations for either H^+ or Na^+ in regard of the experiments. Both methodologies followed the same protocol. The slurry solution (5g of clinoptilolite and 1L of solution) was stirred for 2 hours followed by 10 min centrifuging at 4500rpm. The supernatant was discarded and the settled fine grains were then mixed with fresh solution of HCl or NaCl, respectively. This process was carried out six times, after which no significant amount of interfering cations (e.g. Mg^{2+}) was released into the supernatant. Finally, the conditioned fine grains were dried at 100°C for 24h.

Adsorbent characterization

The adsorbent was characterized for its adsorption surface area and its micropore volume. Adsorption surface area was determined by Brunauer-Emmett-Teller (BET) method using a Micromeritics Tristar 3000 Surface area and Porosity Analyser (Micromeritics, The Netherlands). Micropore volume was characterized using the t-plot micropore method [32]. Three replicates were determined.

2.2.3 Mixed matrix membranes

Membranes preparation

The preparation of the membranes was carried out following a procedure already established [29]. Different amounts of grinded and conditioned clinoptilolite were blended into mixtures of 15wt.% PSf and 10wt.% PVP in NMP. The resulting blends had a concentration in clinoptilolite of 0wt.%, 25wt.%, 50wt.% and 70wt.%. A blend of 75wt.% of clinoptilolite was also produced, but it resulted in very brittle membranes and it was thus discarded. The blends were stirred for 1h and afterwards sonicated for 1h to disperse the fine grains. This process was repeated three times and the slurry was left overnight under stirring to achieve a homogeneous suspension. The polymeric solution was casted on a flat glass plate with a 500μm casting knife (Zehntner ZAA 2300, Germany) and afterwards it was immediately submerged in a water bath at 60°C forming a porous membrane.

Membrane characterization

Thickness and porosity

A thickness gauge was used to measure the average thickness of each of the membranes. Porosity (ε) was determined by the water uptake of a piece of dry membrane with an identified mass. Three pieces of each of the membrane compositions were used to calculate the average porosity.

Porosity (ε) was calculated according to (1):

$$\varepsilon(\%) = \frac{m_{wet} - m_{dry}}{m_{wet}} x100 \quad (1)$$

where m_{dry} and m_{wet} are the mass of the dry membrane and the mass of the swollen membrane (water uptake) after 24h in a water bath at room temperature, respectively. Before weighing m_{wet}, an adsorbent paper was used to remove the water film around the MMM.

Morphology

Scanning Electron Microscope (SEM) analysis was carried out to visualize the cross-sectional and perpendicular areas of the casted membranes. MMM were submerged in liquid nitrogen and fractured for neat observations. A gold spatter coating was applied on the membranes using a Jeol JFC-1200 Fine Coater (The Netherlands) and membranes were scanned by a Jeol JSM-6480LV Scanning Electron Microscope (The Netherlands).

2.2.4 Adsorption capacity

The adsorption capacity of the zeolite was tested in a static manner and the adsorption capacity for MMM was tested in two manners: static and dynamic. The static manner consisted on batch experiments were the solution remained constant during the test whilst in the dynamic manner the solution flowed through the membrane. Three replicates were carried out for each experiment.

Static adsorption capacity

The static adsorption capacity of clinoptilolite was tested by batch experiments in which 0.5g of fine grains or 45cm² of MMM were added to 100mL of solutions of $NaNO_3$, KNO_3 and NH_4NO_3 in different

concentrations (0.1mM to 4mM). The heterogeneous mixture was continuously stirred. The adsorption capacity of cations was calculated according to (2):

$$q_i = \frac{n_{i,initial} - n_{i,equilibrium}}{\text{mass zeolite}} \quad (2)$$

where q_i ($mmol_i\ g_{zeolite}^{-1}$) is the adsorption capacity at equilibrium, $n_{i,initial}$ (mmol) is the amount of cations in solution at the start of the experiment and $n_{i,equilibrium}$ (mmol) is the amount of cations in solution at the equilibrium of the experiment.

Dynamic adsorption capacity

The dynamic adsorption capacity was assessed for the MMMs. The performance was measured at a constant pressure (0.5bar) using a stirred dead-end filtration cell with a capacity of 400mL. The membranes were tested individually and had an effective membrane area of $45cm^2$. The permeability of the membrane was 17.8mL $h^{-1}\cdot cm^{-2}\cdot bar^{-1}$. 100mL feed solutions was filtered over the membrane and effluent samples were taken in time. The amount of cation adsorbed was calculated by numerical integration of the measured ion concentration in the effluent.

Removal efficiency

The removal efficiency of clinoptilolite (R_i)(-) (%) for each of the cations was used to calculate the relative removal efficiency ($R_{i,j}$)(-) which describes the selectivity of clinoptilolite according to (3) and (4):

$$R_i = \frac{n_{i,initial} - n_{i,equilibrium}}{n_{i,equilibrium}} \times 100 \quad (3)$$

$$R_{i,j} = \frac{R_j}{R_i} \quad (4)$$

where R_j(-) is the removal efficiency of component *j* and R_i(-) is the removal efficiency of component *i*.

Desorption capacity

The desorption capacity was tested for a MMM containing 70wt.% of clinoptilolite previously tested for its static and dynamic adsorption capacity at 1mM of equimolar solution of Na^+, K^+ and NH_4^+. The desorption capacity was investigated in a 24h batch experiment using 1.0M HCl (100mL) at room temperature and ultrapure water (100mL) at 60°C under stirring conditions. Ultrapure water at room temperature was also assessed, however no desorption was observed. The aim was to recover the adsorbed cations and to restore the homoionic condition in the clinoptilolite structure. The desorption capacity was calculated according to (5):

$$\delta_i = \frac{n_{i,24h} - n_{i,water}}{n_{i,adsorbed}} \times 100 \qquad (5)$$

where δ_i(-) (%) is the desorption capacity of clinoptilolite for cation *i*, $n_{i,24h}$ (mmol) is the amount of cation *i* in solution after 24h of the experiment, $n_{i,water}$ (mmol) is the amount of cation *i* in water at the beginning of the experiment and $n_{i,adsorbed}$ is the amount of cation *i* adsorbed during the adsorption experiment.

2.2.5 Analyses

The concentration of K^+, Na^+ and NH_4^+ was determined by ion-chromatography (IC, Metrohm Compact IC 761) with a confidence level <5%. Proton (H^+) exchange was measured via pH variation using a pH-meter (Metrohm 827 pH lab).

2.3 Results and discussions

The removal of Na^+ (non-adsorption) from diluted urine as well as the recovery of K^+ and NH_4^+ (adsorption and desorption) was assessed according to morphological properties of clinoptilolite in fine grains and in MMM as well as adsorption and desorption capacity determined with synthetic solutions and a diluted urine matrix.

2.3.1 Adsorbent characterization

We characterized clinoptilolite in fine-grained form for its adsorption surface area and pore volume, particle size and its adsorption capacity regarding two different conditioning processes.

Adsorption surface area and micropore volume

The BET surface area (BET) was determined for clinoptilolite in form of fine grains (after grinding) and in form of grains. Fine grains presented a BET of 25.97±2.01 $m^2 \cdot g^{-1}$ whilst grains had a BET of 18.98±1.56 $m^2 \cdot g^{-1}$. The higher BET of fine grains indicates that grinding the clinoptilolite grains improved the availability of adsorption sites. The pore volume for both forms of clinoptilolite was in the range of 4.20±0.53 $mm^3 \cdot g^{-1}$. The average pore size measured in the fine grains (9.44±0.21nm) was also greater than the average pore size measured in the grains (7.61±0.17nm). We therefore use the clinoptilolite in form of fine grains in the production of MMM.

Particle size of fine grains

The analysis of the particle size distribution of the fine grains showed that around 23% of the particles presented a diameter around 0.5μm. The rest of the particles are homogeneously distributed in diameters greater than 0.5μm and smaller than 10μm (Figure 1).

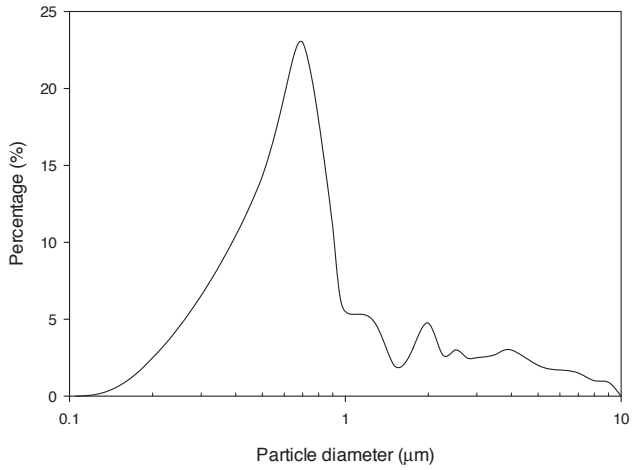


Figure 1. Distribution (%) of the particle size (μm) of grinded clinoptilolite.

2.3.2 Membrane characterization

Mixed matrix membranes containing amounts of clinoptilolite in fine grain from 0 to 70wt.% were successfully produced. Their morphological characterization was based on thickness, porosity and scanning electron microscopy to analyze the distribution of the fine grain in the polymeric matrix.

Thickness and porosity

Table 2 shows the thickness and the porosity of the produced MMM regarding the amount of clinoptilolite incorporated. The thickness of MMMs increases as the amount of clinoptilolite increases. When no clinoptilolite is present (0wt.%) the thickness is around 209±8.3 μm and it reaches up to 231±9.5 μm at 70wt.% of clinoptilolite in the MMM. The presence of clinoptilolite expands the polymeric matrix and therefore increases the thickness of the MMM, but also it decreases the porosity (ε) due to the occupation of pores in the polymeric structure by the clinoptilolite. Porosity

was 79% when the amount of clinoptilolite was 0wt.% and it reduced to 53.9% when the amount was 70wt.%.

Table 2. Thickness and porosity of MMM as to their amounts of zeolite

Amount clinoptilolite (wt.%)	Thickness (μm)	Ɛ (-) (%)
0.0	209 ± 8.3	79.2 ± 1.4
25	225 ± 12	73.2 ± 1.7
50	223 ± 10	65.6 ± 2.9
70	231 ± 9.5	53.9 ± 1.3

Morphology

Figure 2 shows cross-section images of MMMs depending on the amount of clinoptilolite: A and B, 0wt.%; C and D 25wt.%; E and F, 50wt.%; G and H, 70wt.%. Images on the left (A, C, E and G) have a magnification of 400 times to analyze the homogeneity of the membranes and the macrostructure of the MMMs. Images on the right (B, D, F and H) have a magnification of 2000 times to observe the attachment of the fine grains into the polymeric matrix. Clusters of clinoptilolite are not observed in the images on the left of Figure 2 although in image G (70wt.%) particles tend to be more aggregated. The images on the left show the presence of macropores and micropores in the structure of the membranes due to the formation process of the MMMs. However, as the amount of clinoptilolite increases, a decrease of the pore structures is observed. This fact is consistent with our measurements on the porosity of the MMMs. The images with a magnification of 2000 times (right column) show that clinoptilolite is closely entangled with the polymer but it does not cover the zeolite structure. The polymer could have an influence on adsorption capacity of the clinoptilolite as it could obstruct the pores of the clinoptilolite.

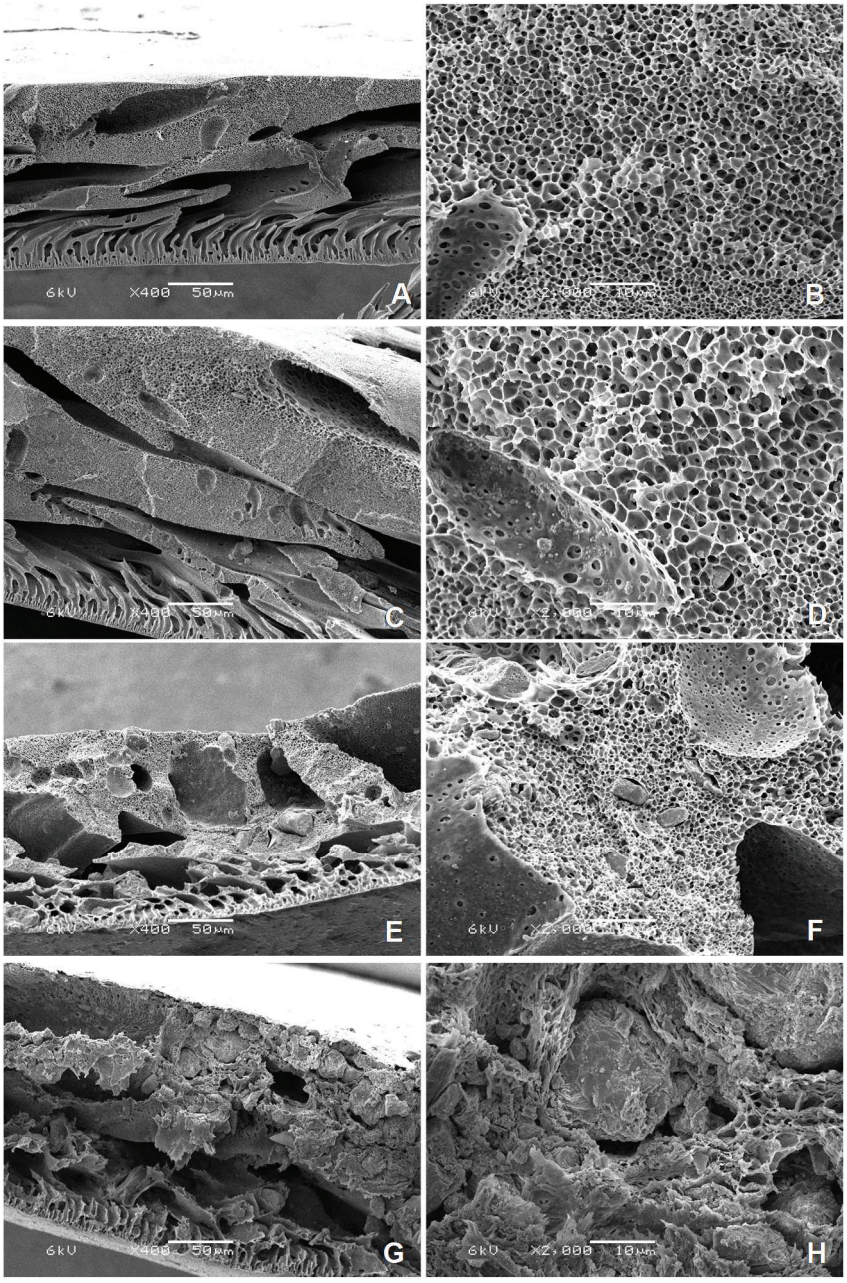


Figure 2. SEM images of cross-section of MMM with different compositions: A and B, 0wt.%; C and D, 25wt.%; E and F, 50wt.%; G and H, 70wt.%. Images on the left have a magnification of 400. Images on the right have a magnification of 2000.

2.3.3 Static adsorption capacity

Adsorbent

There are two main methodologies to condition zeolites to make them homoionic: either using an acidic solution (HCl) [33] or a solution of sodium chloride (NaCl) [34]. We studied which methodology is better to remove Na^+ (avoid further adsorption in case of NaCl conditioning) and adsorb K^+ and NH_4^+ using solutions of 1.0M HCl and 1.0M NaCl. Both methodologies followed the same protocol. The adsorption capacity of clinoptilolite in fine grain for each of the three cations (K^+, Na^+ and NH_4^+) was assessed in regard of the conditioning process. Tests were carried out with single salt solutions and with mixed salts solutions to evaluate the adsorption capacity of each of the cations and also to study the capacity in case of competitive ions.

Single salt tests

Single salt solutions of KNO_3, NH_4NO_3 or $NaNO_3$ with a concentration of 0.1 to 4.0mM were used to study adsorption capacity and the influence of the conditioning methodology. Figure 3 shows the adsorption capacity of clinoptilolite for K^+ and NH_4^+. Na^+ is not represented because its concentration increased in time: Na^+ was released from the fine grains, not adsorbed for both types of conditioning. Fine grains conditioned in NaCl presented a higher adsorption capacity (0.5 $mmol \cdot g_{zeolite}^{-1}$) than fine grains conditioned in HCl (0.1-0.2 $mmol \cdot g_{zeolite}^{-1}$) for K^+ and NH_4^+. This fact was experienced before by Wang and Peng [14] and by Rozic *et al.* [35] who showed that the use of acidic solutions for homogenizing the cation content in clinoptilolite resulted in a reduction of the cation-exchange capacity due to the loss of Al^{3+} in the zeolite structure. Although the use of acid solutions is valuable in order not to further add the cations under study in our experiments, we decided to condition clinoptilolite with NaCl in our following experiments and considered the extra Na^+ added.

Besides the conditioning process, the static adsorption capacity achieved with clinoptilolite is very dependent on its natural origin. Wang and Peng [14] reviewed the adsorption capacities of several clinoptilolites regarding their origin. For example, Lei *et al.* [36] reported that clinoptilolite with highest static adsorption capacity of NH_4^+ can be achieved by microwave treatment of the Chinese zeolite reaching an adsorption capacity of 1.7 $mmol \cdot g^{-1}$. In our study, we used clinoptilolite from Croatia which has the same origin as the one used by Rozic *et al.* [35] and Farkas *et al.* [37]. In this study, we achieved an adsorption capacity of 0.5 $mmol \cdot g_{zeolite}^{-1}$ which is in the range of their reached NH_4^+ adsorption values: 0.43–0.76 $mmol \cdot g_{zeolite}^{-1}$.

Relative removal efficiencies of K^+ over NH_4^+ (R_{K,NH_4}) are shown in Table 3. $R_{K,NH4}$ for NaCl remained around 1 which indicated that the removal of NH_4^+ and K^+ was about the same for both cations. In the case of HCl, $R_{K,NH4}$ decreases as the initial concentration increases. This dependence could be related to ionic strength and therefore the competition and affinity of the cations to be adsorbed in the clinoptilolite structure possibly altered by the effect of the acidic conditions [20, 38].

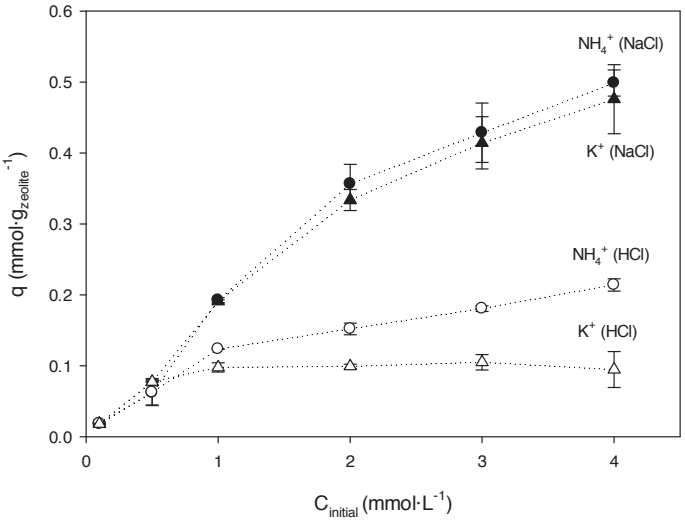


Figure 3. Adsorption capacity of clinoptilolite in fine grains conditioned in NaCl and HCl using single salt solution.

Table 3. Relative removal efficiency of K^+ over NH_4^+ regarding the conditioning process of clinoptilolite in fine grains in single salt solutions.

$C_{initial}$ (mmol·L^{-1})	$R_{K,NH4}$ (-) in HCl	$R_{K,NH4}$ (-) in NaCl
0.1	0.99	1.06
0.5	1.24	1.01
1.0	0.79	0.99
2.0	0.65	0.94
3.0	0.58	0.97
4.0	0.44	0.95

The mass balance between cations removed from the solution and the cations released by clinoptilolite was evaluated to understand the exchange process when NaCl was used during conditioning. Figure 4 illustrates the relation between the adsorption of K^+ and NH_4^+ and the amount of Na^+

released. The dashed line corresponds to the parity plot. A regression analysis was performed with a linear fitting (y = ax + b) to relate between the adsorbed K^+ and $NH_4^+$and the released Na^+. A slope ("a" in y = ax + b) close to 1 and therefore close to the parity plot indicates that there was a 1:1 ion exchange. For K^+ the slope is 1.07 (R^2 = 0.995) and for NH_4^+ is 1.05 (R^2 = 0.996). These results indicate that Na^+ in the structure of clinoptilolite is exchanged by either K^+ or NH_4^+.

The mass balance could not be determined during experiments with HCl conditioning, because the amount of proton release was too low to be accurately measured.

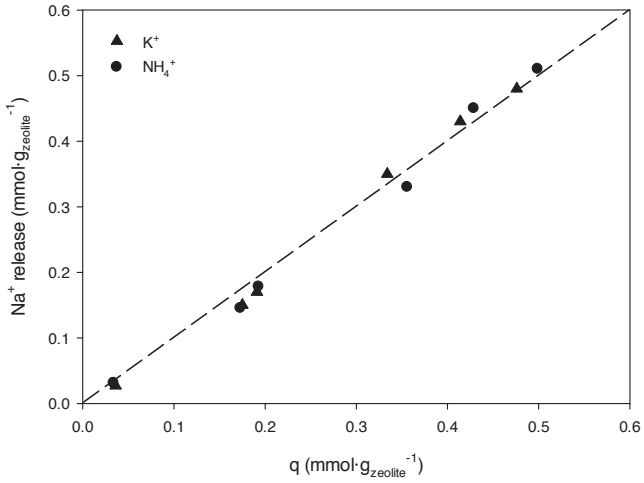


Figure 4. Adsorption capacity of clinoptilolite in fine grains conditioned with NaCl over the amount of Na^+ released including parity plot (dashed line).

Mixed salts tests

The adsorption capacity of clinoptilolite in fine grains conditioned with NaCl for K^+ and NH_4^+ in the presence of the other competitive cations was determined using equimolar mixtures of KNO_3, NH_4NO_3 and $NaNO_3$. Figure 5 shows the adsorption capacity of clinoptilolite for K^+ and NH_4^+. In the presence of competitive cations, clinoptilolite had a higher affinity for K^+ than NH_4^+. The total adsorption capacity ($q_K + q_{NH4}$) determined is comparable to the results obtained from the single salt experiments. It is about 0.5 $mmol \cdot g_{zeolite}^{-1}$ for clinoptilolite conditioned with NaCl.

The relative removal efficiencies of K^+ over NH_4^+ ($R_{K,NH4}$) are shown in Table 4. $R_{K,NH4}$ increased with the presence of competitive ions in the mixture. The higher the initial concentration was, the higher the removal efficiency for K^+. Jorgensen *et al.* [20, 39] and Rozic *et al.* [35] associated the decrease of NH_4^+ adsorption when its initial concentration increased with the certain dissociation of NH_4^+ into NH_3 because the pH of ultrapure water (pH 4.40) increases when salts are added (pH 6.81-7.82). This could lead to an adsorption of H^+ instead of NH_4^+ because of the amphoteric character of clinoptilolite as Rivera *et al.* [40] and Guo *et al.* [41] also experienced. H^+ is being adsorbed by clinoptilolite to neutralize the aqueous medium and the adsorption of NH_4^+ not dissociated is lower as K^+ is as well adsorbed, contrary to the single salt experiments.

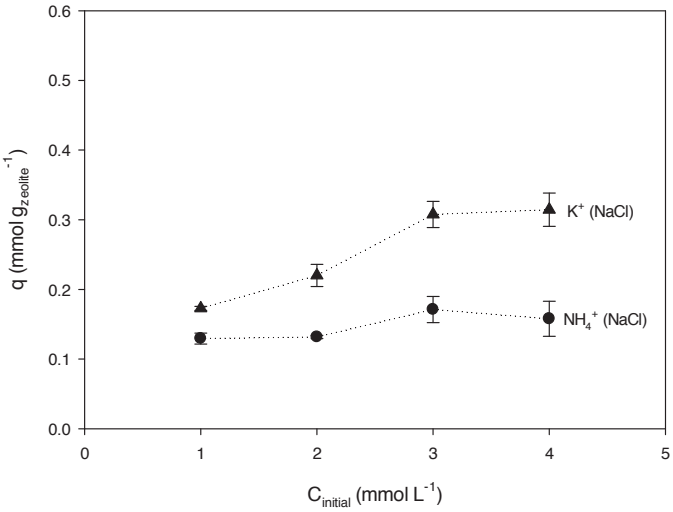


Figure 5. Adsorption capacity of clinoptilolite in fine grains conditioned in NaCl using mixed salts solution.

Table 4. Relative removal efficiency of K^+ over NH_4^+ of clinoptilolite (conditioned in NaCl) in fine grains in mixed salts solutions.

$C_{initial}$ (mmol·L^{-1})	$R_{K,NH4}$ (-) in NaCl
1.0	1.33
2.0	1.36
3.0	1.80
4.0	1.90

In this case, there was also a release of Na^+ and the linear fitting curve had a slope of 1.13 (R^2=0.925) confirming an ion-exchange process.

Mixed matrix membranes

The adsorption capacity of the synthesized MMMs (0, 25, 50 and 70wt.% clinoptilolite) was tested for solutions containing equimolar amounts of the three cations under study (Figure 6). We studied the effect of the amount of clinoptilolite present in the MMM and the effect of competitive cations on the adsorption capacity. Consistently with previous results, Na^+ exchanged for the adsorbed cations. MMM with 0wt.% clinoptilolite load did not show any adsorption of cations.

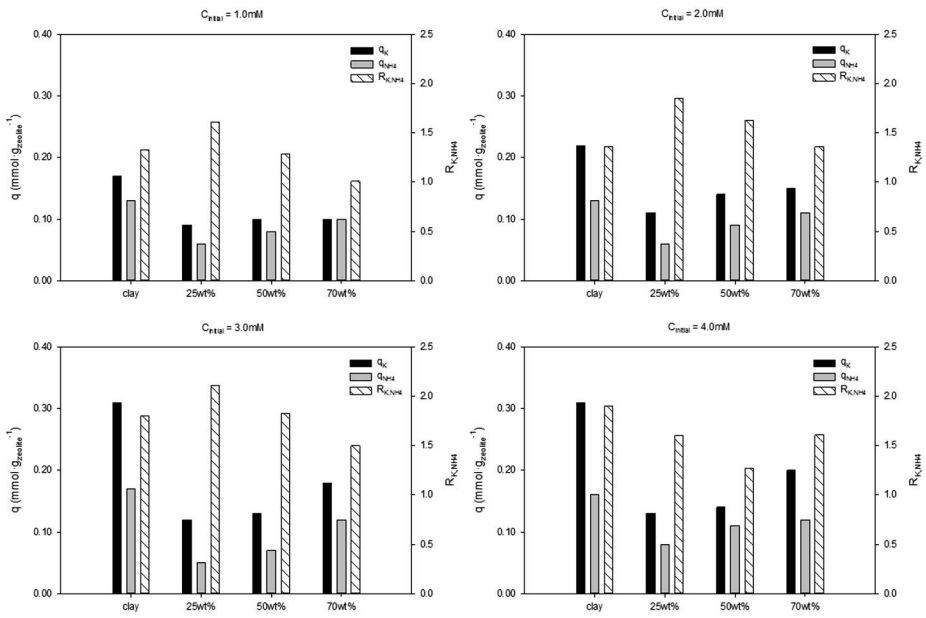


Figure 6. Relation between the amount of clinoptilolite in MMM, the initial mixed concentration and the adsorption capacity (q, mmol·$g_{zeolite}^{-1}$) for K^+ and NH_4^+ compared to fine grains and their corresponding R_{KNH4}.

The results showed that the adsorption capacity of the synthesized membranes increased as the amount of clinoptilolite increased. For example, when the initial concentration of each of the cations is 3.0mM the adsorption capacity for K^+ is 0.12 mmol·$g_{zeolite}^{-1}$ when the amount of clinoptilolite is

25wt.% and 0.18 mmol·$g_{zeolite}^{-1}$ when the amount is 70wt.%. The higher the amount of clinoptilolite present in the MMM, the lower is the amount of the polymer mixture. Thus, the more available the clinoptilolite is, the higher is the adsorption capacity. However, the higher the amount of clinoptilolite, the lower is the $R_{K,NH4}$, even lower than clinoptilolite in fine grains. This could suggest that due to the increase on the availability of clinoptilolite, NH_4^+ not dissociated is more probable to be adsorbed and therefore $R_{K,NH4}$ decreases.

2.3.4 Dynamic adsorption capacity

The dynamic adsorption capacity of one MMM containing 70wt.% of clinoptilolite was studied at 0.5bar using a synthetic solution containing 1mM of Na^+, K^+, and NH_4^+ to minimize the effect of NH_4^+ dissociation and with fresh urine (Table 5) 40 times diluted to achieve an NH_4^+ concentration of around 1mM.

Synthetic solution

The maximum adsorption capacity for K^+ and for NH_4^+ (0.2 mmol·$g_{zeolite}^{-1}$) was reached after 5 minutes of experiments (Figure 7) and was two times greater than for batch experiments (Figure 6). This suggests that the application of pressure enhances the adsorption of the cations into the clinoptilolite as cations can encounter easily the inner particles of clinoptilolite inside the pores of the MMM. Measurements showed no adsorption of Na^+.

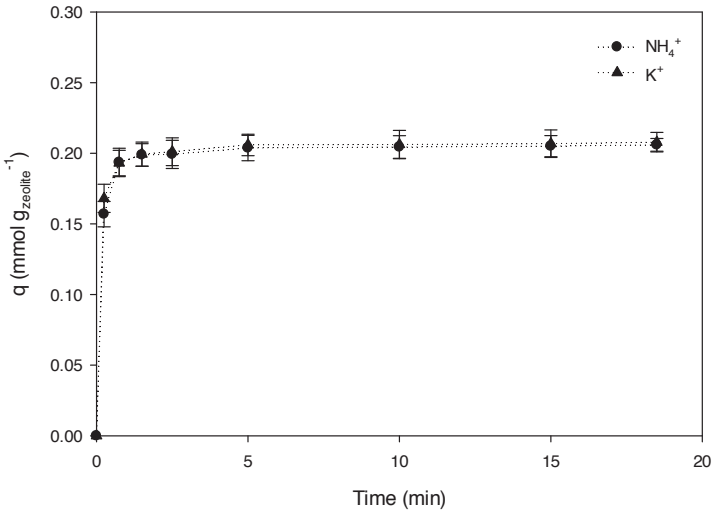


Figure 7. Dynamic adsorption capacity of MMM with 70wt.% of clinoptilolite for K^+ and NH_4^+ at 0.5bar of a synthetic sample.

Diluted urine matrix

The separation of Na^+ from K^+ and NH_4^+ was tested with a sample of diluted fresh urine to assess the MMM (70wt.%) performance with a non-synthetic sample containing a more complex matrix. The initial concentration of urine for the cations of interest was as shown in Table 5. Naturally, the cation in the highest concentration is Na^+ followed by K^+ and then NH_4^+. The fresh urine sample was diluted 40-fold to have cation concentrations in the same range as previous experiments.

Table 5. Initial cation concentration of fresh urine.

	$C_{initial}$ (mmol·L^{-1})
NH_4^+	39.7±1.1
Na^+	157±5.7
K^+	86.5±2.4

Similarly, as the dynamic tests with a synthetic solution, the maximum adsorption capacity for K^+ is around 0.2 mmol·$g_{zeolite}^{-1}$ (Figure 8). However, the adsorption capacity for NH_4^+ is around 0.03 mmol·$g_{zeolite}^{-1}$ lower. This could be explained by the initial concentration of K^+, which is two times higher than the NH_4^+ concentration and therefore the availability of K^+ to be adsorbed is greater.

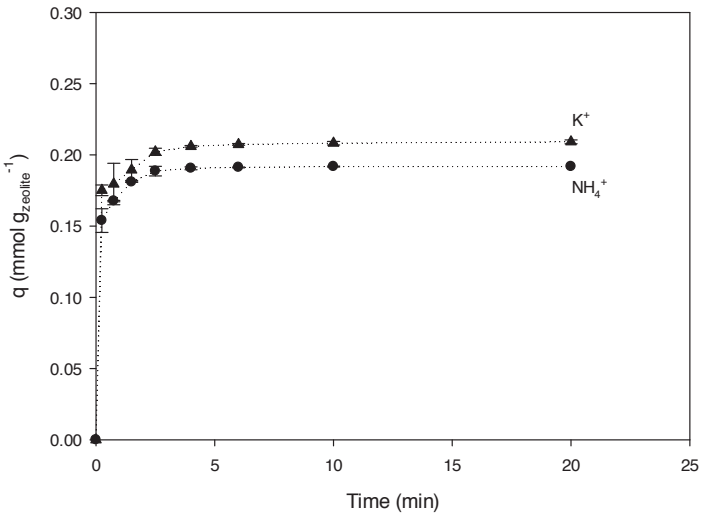


Figure 8. Dynamic adsorption capacity of MMM with 70wt.% of clinoptilolite for K^+ and NH_4^+ at 0.5bar of urine sample.

2.3.5 Desorption capacity

In order to recover the adsorbed nutrients (K^+ and NH_4^+), it is necessary to exchange them for another cation. Recovery of the adsorbed cations and therefore regeneration of clinoptilolite is mainly performed by brine treatment [12, 15] or by caustic treatment [42]. These processes involve an addition of a cation (e.g. Na^+) to the mixture of the recovered nutrients. Because our purpose is to recover, an addition of a cation is not convenient. Therefore, we studied the exchange of H^+ with the adsorbed K^+ and NH_4^+ from MMM. Two methodologies were used: 1.0M HCl at room temperature and ultrapure water

at 60°C. The desorption capacity of clinoptilolite (δ_i) was tested for a MMM containing 70wt.% of clinoptilolite previously used in static and dynamic adsorption capacity experiments using 1mM of equimolar solution of Na^+, K^+ and NH_4^+. As shown in Figure 9, the desorption of both cations is higher using temperature than an acidic solution. Desorption is greater for higher temperatures due to an increase in solubility [40]. Moreover, acidic treatments deteriorate the chemical structure of clinoptilolite [14]. For both desorption methodologies, the desorption of NH_4^+ is greater than K^+ after 24h. This fact could be associated to the higher affinity of clinoptilolite for K^+. Therefore, a fraction of the adsorbed K^+ remains in the structure of clinoptilolite [42]. In the case of a continuous process, the fact that nutrients remain in the structure of the clinoptilolite could be a drawback as the ion-exchange might be affected and therefore the adsorption capacity can diminish in each run.

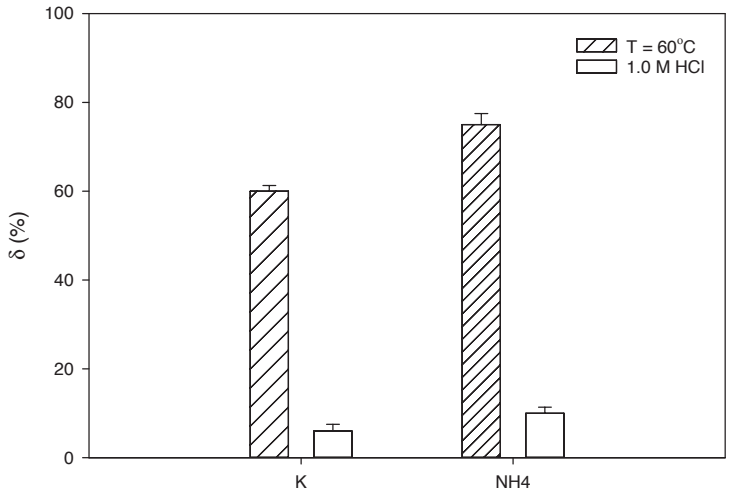


Figure 9. Desorption of K^+ and NH_4^+ of a MMM (70wt.%) after 24h of desorption experiment using 1.0M HCl or ultrapure water at 60°C.

2.4 Conclusions

We showed that MMMs containing clinoptilolite are a promising alternative to recover K^+ and NH_4^+ and to separate them from Na^+.

From both conditioning processes tested, for NaCl, $R_{K,NH4}$ was around 1 and for HCl, it decreased as the initial concentration of the cations increased. The effect the acidic conditions have in the chemical structure of clinoptilolite might change its affinity for the studied cations.

We successfully produced 3 types of MMM with different amounts of clinoptilolite: 25wt.%, 50wt.% and 70wt.%. The latter amount (70wt.%) presented the highest static adsorption capacity. $R_{NH4,K}$ was comparable to clinoptilolite in fine-grained form, but adsorption capacity per mass of clinoptilolite was reduced to half because of the presence of the polymeric matrix around the surface of the clinoptilolite.

Dynamic adsorption with a synthetic solution achieved a $R_{NH4,K}$ very close to 1 suggesting that the pressure driven experiment benefited the contact between the adsorption sites and the non-dissociated NH_4^+. In the case of diluted urine, the system showed the same adsorption capacity for K^+ and slightly lower for NH_4^+ due to a different initial concentration.

The separation of Na^+ from synthetic solutions (either containing salts or mixed salts) and diluted urine was successfully achieved by clinoptilolite in form of fine grains and embedded in MMM. No adsorption of Na^+ was observed after the conditioning processes (HCl and NaCl) of the fine grains in either static or dynamic adsorption tests. Therefore, clinoptilolite is a good choice for the separation of Na^+ from the nutrients.

The highest recovery of K^+ and NH_4^+ was achieved with ultrapure water at 60ºC with a recovery of 60 % of the K^+ and 75% of the NH_4^+. The difference of the recovery of the two cations was attributed to solubility.

We suggest further research needs to be conducted with undiluted urine.

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